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A Thesis
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Requirements for the Degree of
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C O N T E N T S

I L L U S T R A T I O N S

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INTRODUCTION

Although there is no standardized list of alloys nor any universally used nomenclature, most investigators have, to avoid confusion, concurred in at least grouping the metals under several general heads -- the precious metals: gold, silver and the platinum group; the light metals: aluminum and magnesium; the non-ferrous metals (excluding all steels and iron-base alloys); the antifriction metals, etc. Furthermore, although many metals would naturally fall under such a general descriptive term as "white metal" (gold and copper are the only common metals to have any decided color), most of these metals have more outstanding characteristics than their possession of mere white color and hence can only properly fall in another classification. Notwithstanding the fact that many or all of the five metals also fall in other groupings, because of their similarity from either a physical or chemical standpoint, or both, the white metals are: lead, antimony, tin, bismuth and cadmium.

In general, the white metal group is characterized by the high densities, low melting points (seldom over 400° C.) and the very limited solid solubility of the alloys comprising it.

It was the purpose of the work entailed in the composition of this thesis to investigate various of the properties of certain of these white metal alloys.

EXPERIMENTAL PROCEDURE

Each of the alloys was made up from the pure metals. Constituent metals were weighed out in the desired percentages into 25-gram charges.

To minimize any discrepancies which may have been caused in the alloy's composition by oxidation of either or both constituents, each charge was given a cover after placing the metals in a large annealing cup for melting. Two covers were tried-- borax glass and common lard. The latter material (as fat) is used in foundry practice. On being strongly heated it decomposes and evolves a considerable quantity of gas which exerts a protecting influence on the surface of the metals; also, when gas evolution has ceased, a layer of very finely divided carbon remains and acts efficiently in preventing oxidation. Further, although borax glass combines with the fused metals to a slight extent, no combination with carbon may be feared and hence lard was found to be the more satisfactory covering material. The cups were capped with a refractory crucible cover during the melting period.

All alloys were stirred while molten with a graphite rod and all were cast in a cast-iron mold (some slowly and some quickly cooled--see the following). The mold dimensions were: 8 x 0.75 x 0.5 cms. -- the long, narrow ingot from this was found to be suitable for all subsequent tests. Micrographical specimens and hardness test-pieces were sawed from the ingot in centimeter lengths.

Since one procedure of testing was not applicable to all alloys because of the great difference of certain properties (chiefly hardness and brittleness), the results obtained and some of the experimental factors noted will be treated individually for each alloy.

Nor ternary or quaternary alloys were made up for investigation in this work, although the field in which they fall should be of much interest because of the very fusible alloys which are found there. Those binary alloys were chosen which seemed to be of the most interest either because of their extensive commercial use or because their compositions placed them in an interesting field of their respective equilibrium diagrams.

Melting of the constituent metals to form alloys was accomplished either over the Fisher burner flame or in the small laboratory muffle. (The latter was used only in making the high-melting antimony alloys.) Reducing conditions were obtained in using the burner by forcing a luminous and smoky flame to the exclusion of air. Melting over the burner also allowed for facility in stirring and for noticing when the melt was down and ready for pouring.

As it is in any casting work, the casting temperature for the white metal alloys is a very important factor in the final character of the alloy. If it be cast at too high a temperature the metal possesses the coarse structure of a slowly cooled piece; this, of course, causes the casting to be weak and commercially useless. If the alloy is poured at too low a temperature "cold shuts" result and there is the very undesirable possibility of segregation of the less fusible constituents away from the slower cooling constituents. There is the further danger of inclusions of cover materials which were unable to escape from the viscous mass which exists close to melting points. Logically, the proper temperature of casting would be such that the mould would be completely filled with moulten metal before solidification could begin. It is common practice to allow 100^{o} cooling range (between casting temperature and solidification temperature) for alloys or metals melting around 1000^{o} C. Alloys of lower melting points (which cool slowly) may be treated to advantage, however, if the casting temperature is only slightly above the initial freezing point.

As to the effect of change in the rate of cooling -- in general it may be said that slow cooling produces a large grain, a coarse structure and relatively weak alloys, while rapid cooling gives a fine structure and a stronger, but more brittle alloy.

The specific gravity of an alloy is not proportional to the specific gravities of the metals of which it is made and may not be computed as the arithmetical mean between the numbers denoting the two specific gravities. Instead, the proper relation for calculation exists in the comparative volumes of the constituents.

Algebraically:

$$M = \frac{(W+w)Pp}{Pw+pW} \qquad (1)$$

in which M = specific gravity of the alloy,

W & w = respective weights of the metals present,

and P & p = respective sp. gr. of the metals present.

Hardness Testing

All of the alloys were tested for hardness in the laboratory Shore scleroscope. This instrument measures hardness by the rebound which a miniature, steal-pointed hammer takes when allowed to fall on the specimen from a definite height (about ten inches). With the machine in good shape and with uniformly good specimens, accurate hardness tests may be obtained with dispatch. Test pieces were carefully chosen and prepared so that the smoothest surface and that with the most perfect horizontality would be exposed to the hammer's fall in the machine. Consistently satisfactory results were obtained in the use of this tester.

Microscopy

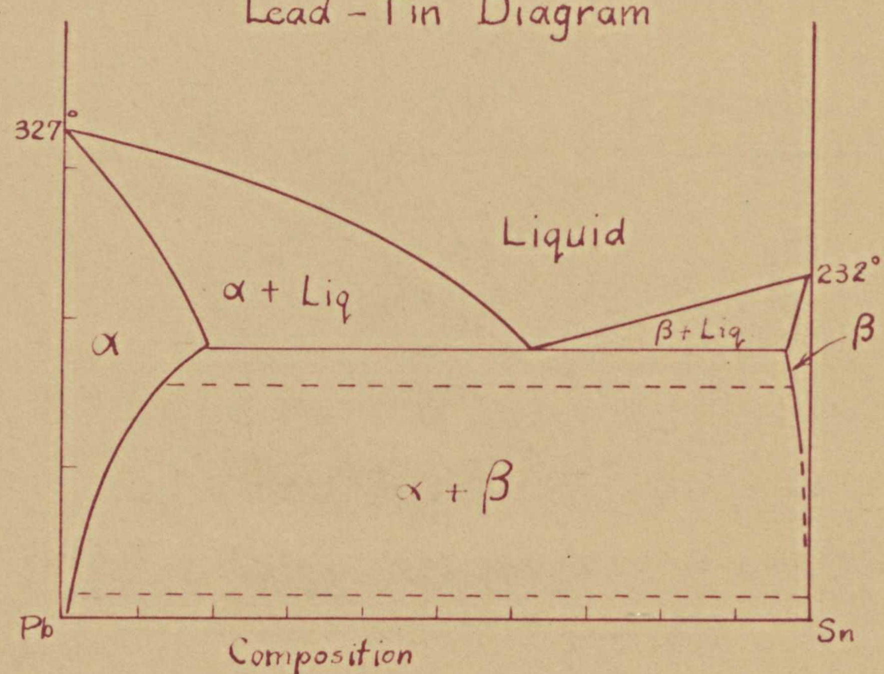
A specimen of each alloy was taken for microscopic examination. The procedure for preparing these was substantially the same for each: the sawed surface was first filed down and then ground to smoothness by successive treatments on No's. 0, 00, 000, 0000 emery paper; wet polishing was done on felt using levigated alumina as abrasive; the final polish was accomplished on clean, wet felt. Some of the very soft alloys (such as those of lead and tin) required further, more careful polishing. These last also required a different technique in etching. The particular procedure used will be described under each alloy individually. Most of the microscopic examinations were made at 400 diameters, and photomicrographs were made of those alloys which appeared to be the most significant.

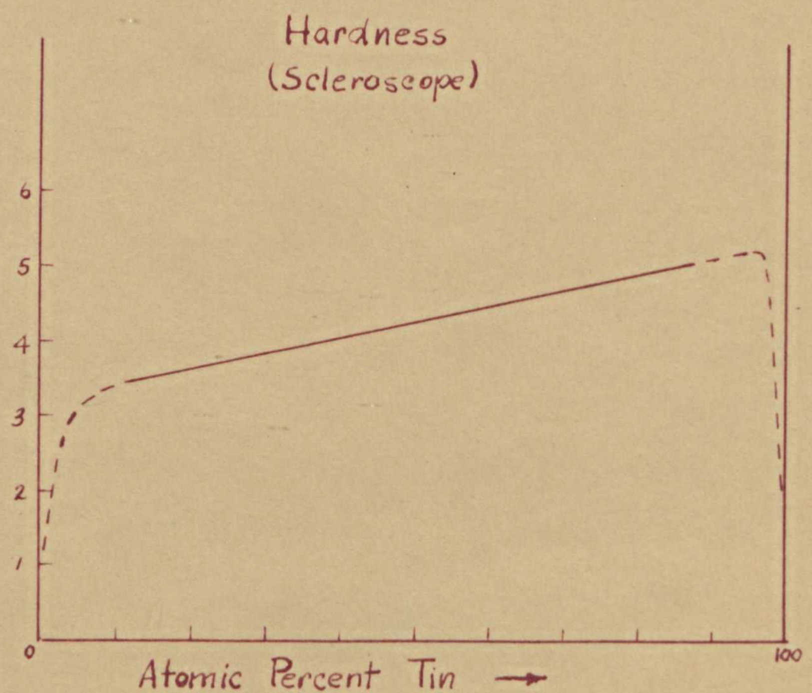
The Lead-Tin Alloys

The extreme softness of pure lead prohibits its very extensive use in the pure state, but it can be hardened by the addition of comparatively small quantities of other metals. The "hardener" appears to exist in the alloy as a eutectic surrounding the grains and stiffening the whole structure. Pure tin is distinguished by its white color and its permanency when exposed to the air. Neither of these characteristics is inhibited by additions of 10 to 15 per cent lead, and the resulting alloys are much harder and cheaper. Also, additions of lead to tin increase its fluidity and castability while molten and its malleability and ductility in solid form. Many of the alloys of lead and tin (notably those around 40% tin) have an especially lustrous appearance, a fact which is taken advantage of commercially in using them for stage jewelry (cast in diamond facets) and for mirrors in reflectors. Perhaps the chief use of the lead-tin alloys is in soldering operations where the 50-50 (plumbers') and the eutectic (tinners') mixtures constitute the majority of soft solders employed. Historically, the most interesting alloy of this group is 82 Sn-18 Pb - pewter- from which a great many utensils and containers were made.

Anticipated difficulty was fulfilled in attempting to get well polished and etched surfaces for microscopy and photomicrography. The alloys are soft, and coarse grinding, instead of removing surface material, merely causes it to "flow". This flowed layer must, of course, be removed to reveal the structure it hides. All emery papers used in grinding these specimens were first smeared with vaseline (this to prevent the metal particles from adhering to the paper and forming a glaze which would drag and distort the surface). Wet polishing was accomplished on clean broadcloth which had been well soaped and held finest levigated alumina for abrasive. The specimen was finished on a clean pad of silk velvet which was well soaked with soap and alumina. After carefully washing the surface to remove all soap, the sample was etched and examined. If the surface was still distorted,

Plate I


Lead - Tin Diagram
327°
232°
Liquid
α + Liq
α
β + Liq
β
α + β
Pb
Sn
Composition


Hardness
(Scleroscope)
6
5
4
3
2
1
0
100
Atomic Percent Tin →

the sample was again polished and etched. This procedure of alternately polishing and etching was repeated until the true structure was satisfactorily revealed.

Data:

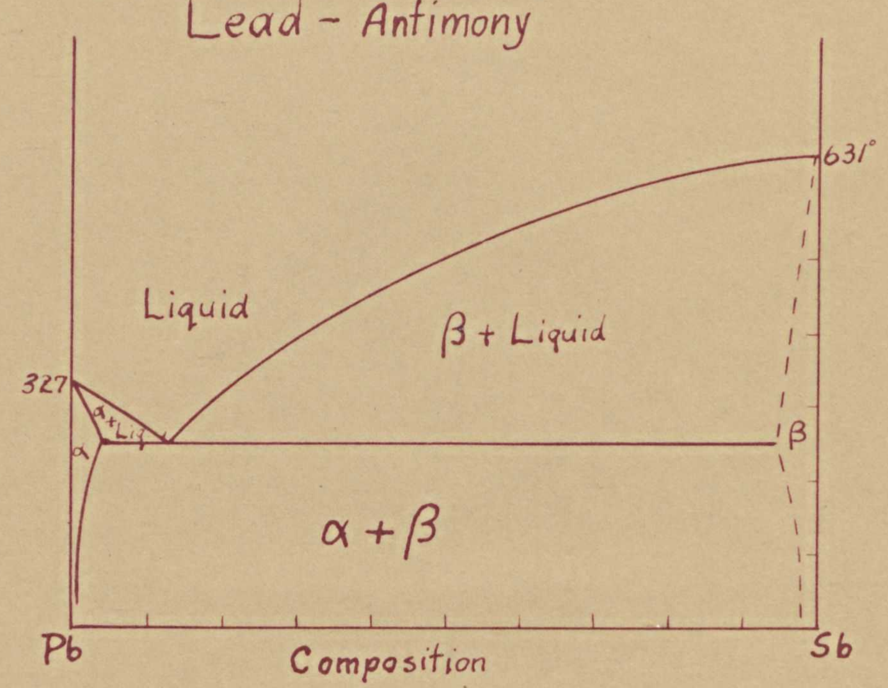
Alloy No.	Lead %	Tin %	Hardness	Atomic% Sn
1	68	32	4	45.5
2	50	50	5	65.6
3	90	10	4	16
4	40	60	5	72.4

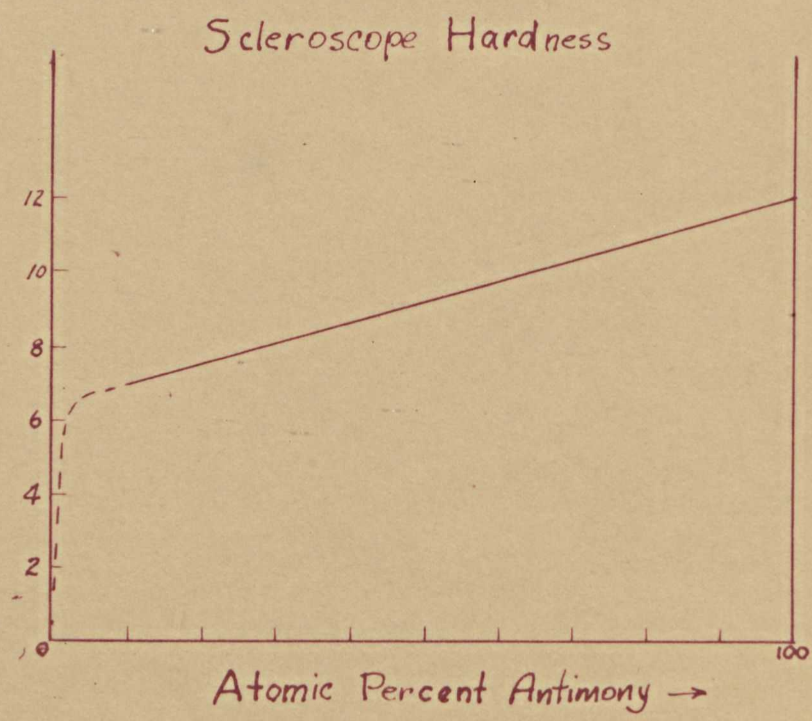
Etchant 0.8% $AgNO_3$- 5 secs.

The Lead-Antimony Alloys

The only alloys of commercial importance in this group are those near the lead side of the diagram. They are used on account of their plasticity, increased hardness and resistance to chemical corrosion as compared to lead, and the ease with which they can be cast or rolled into shape. It was found that alloys which contain more than 10% antimony could not be satisfactorily rolled. Arsenic, incidentally, has the same general effect on the properties of lead. It is very important that lead-antimony alloys be rapidly cooled, lest the primary antimony crystals become forced upwards in the heavier, lead-rich melt and form an antimony-rich upper layer (called bright crust). Such a layer would be quite hard and would give erroneous results on testing. To obviate any such possibility, the antimony alloys were poured into a cold mold and then dumped into a water bath. These alloys were quite hard and required no extraordinary treatment in

Plate II


Lead - Antimony
631°
Liquid
β + Liquid
327
α+Liq
α
β
α + β
Pb
Sb
Composition


Scleroscope Hardness
12
10
8
6
4
2
0
100
Atomic Percent Antimony →

preparation for microscopic examination. Antimony alloys may be made which are twelve times as hard as pure lead, but these find no technical applications because of their great brittleness. Tremendous quantities of hard or antimonial lead (containing 6 to 10 per cent antimony) are used annually in making up such material as type metal, battery plates, tank-liners and anti-friction or bearing metal.

Data:

Alloy No.	Lead %	Antimony %	Hardness	At. % Sb
1	92	8	7	12.8
2	67	33	10	45
3	20	80	11	87
4	77	23	8	34

Etchant 10% Nitric Acid - 5 secs.

Photomicrograph - Alloy No. 2. Segregated plates of antimony in matrix of eutectic.

The Alloys of Lead and Bismuth

Lead and bismuth, when mixed, yield alloys which are malleable and ductile as long as the proportion of bismuth does not exceed that of lead. Malleability and ductility decrease as the bismuth content increases.

Although the bismuth-lead alloys show considerable contraction (maximum at 50-50), the metal bismuth causes the opposite effect, expansion, when mixed into lead-tin alloys (a quality which is made use of commercially as casting

Fig. 1.--67% Lead, 33% Antimony - 400x
Segregated plates of antimony in matrix of eutectic

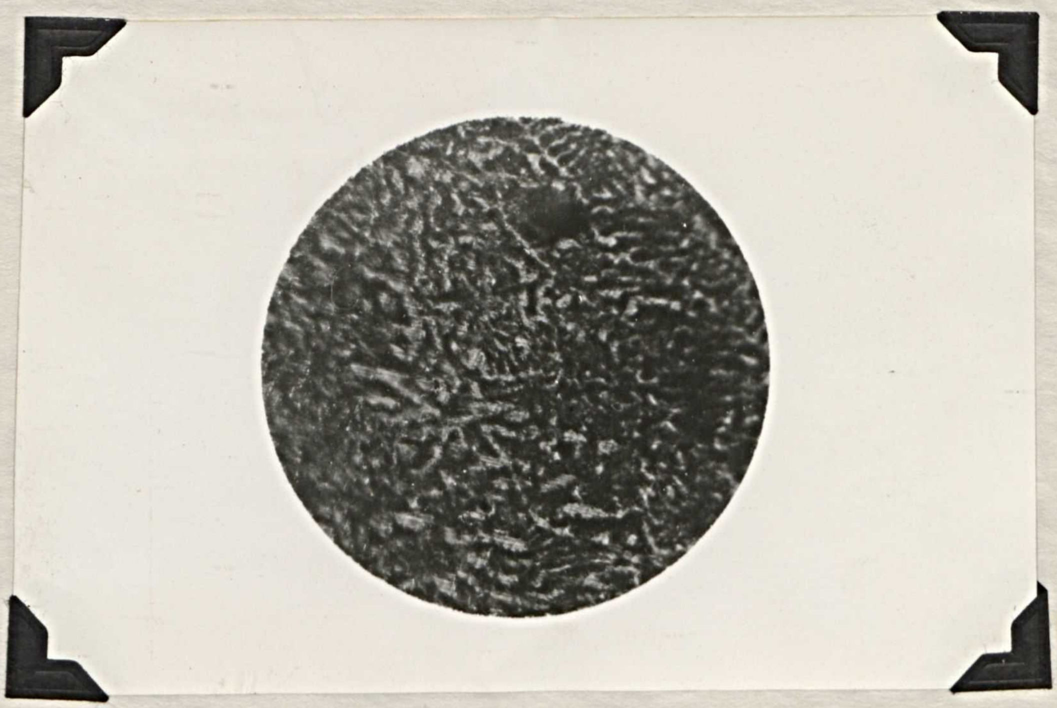


Fig. 2.--40% Lead, 60% Bismuth - 400x
Typical eutectic structure

alloy). Bismuth, when substituted for tin, in a solder gives it the capacity to wet copper and brass. The Bi-Pb-Sn alloy also wets glass and finds extensive use as glass cement.

Chemical grade lead contains 0.1 per cent bismuth which causes the lead to become slightly harder, somewhat crystalline and more fusible, while not affecting malleability. However, the presence of bismuth is so undesirable in lead which is to be used in making white lead that a Bi-content of over 0.0075 per cent prohibits the use of that lead in the manufacture of this product.

Although it was not noted, since work on this thesis did not cover cooling curves, it may be interesting to point out that the action of alloying bismuth and lead is slightly exothermic.

As will be noted from the equilibrium diagram (see Plate IV), the eutectic alloy of 58% bismuth and 42% lead melts at only 125° C. This is the lowest melting binary alloy of the white metal group.

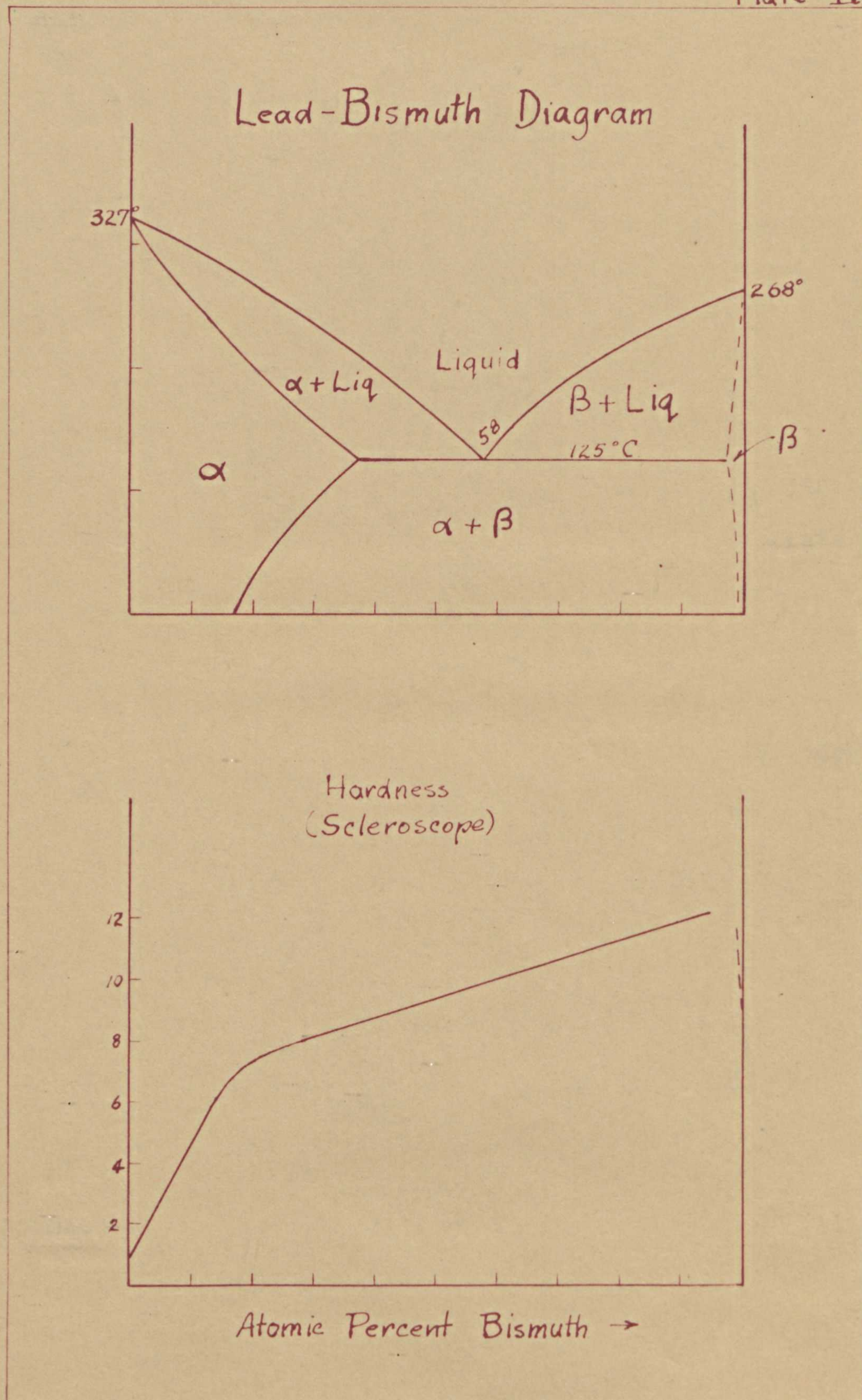
Data:

Alloy No.	Lead %	Bismuth %	Hardness	At. % Bi.
1	70	30	7	29
2	90	10	5	9
3	40	60	10	58

Etchant - Ferric chloride in Conc. Hydrochloric Acid.

Photomicrograph - Alloy No. 3 - delta and beta solid solutions.

Plate IV



Lead-Bismuth Diagram
327°
268°
Liquid
α + Liq
β + Liq
58
125°C
β
α
α + β
Hardness
(Scleroscope)
12
10
8
6
4
2
Atomic Percent Bismuth →

The Alloys of Bismuth and Tin

The binary alloys of tin and bismuth are, in general, rather weak and brittle and for this reason are seldon, if ever, used industrially. Since the alloys are low melters and are very easily made up they are often used in the laboratory for constant-temperature baths. Curiously enough the eutectic between tin and bismuth occurs at the same bismuth-content as that for lead-bismuth (58 per cent). The tin-bismuth eutectic melts at 135° C. Below the eutectic temperature the tin is less able to keep bismuth in solution and a eutectoid inversion takes place at 95° C. (See Plate V.) Below this temperature those alloys which contain up to 98 per cent bismuth are duplex in structure and are made up of pure tin and beta solid solution (see Plate VI, Fig. 1.) Small additions of bismuth to tin increase its hardness, luster and fusibility.

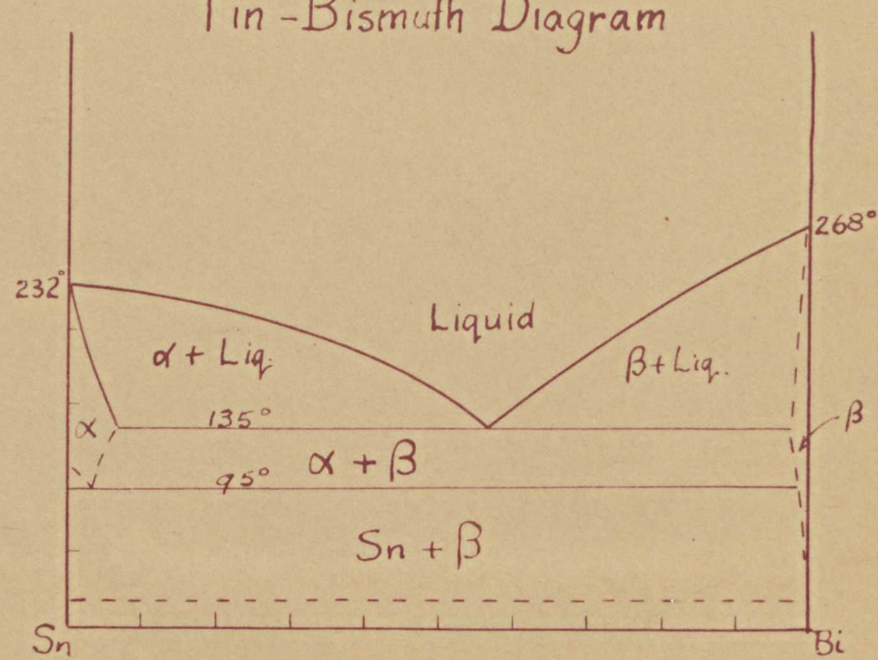
Data:

Alloy No.	Bismuth %	Tin %	Hardness	At. % Bi
1	60	40	7	46
2	80	20	6	69
3	10	90	4	5.7

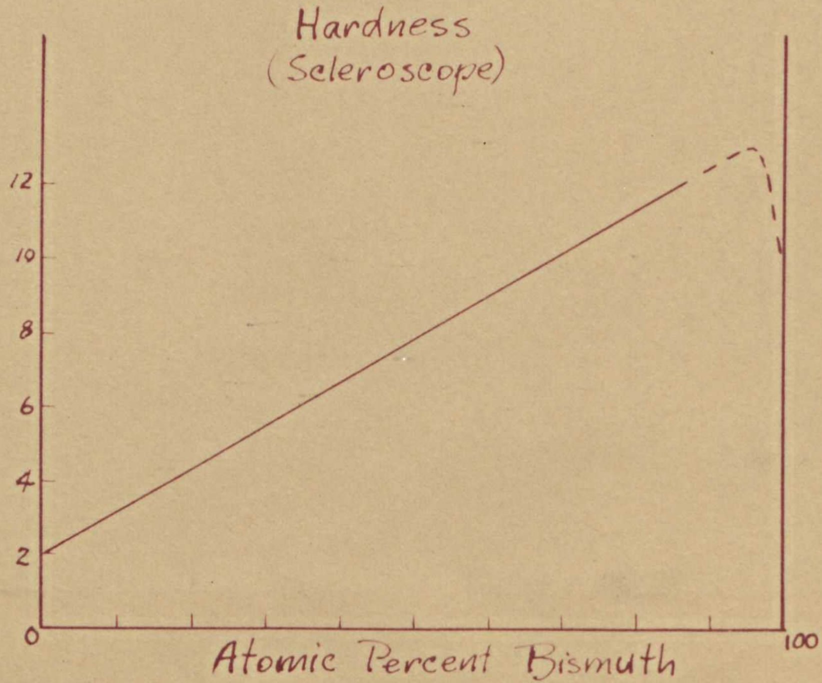
Etchant - Ferric chloride in conc. Hydrochloric Acid.

Photomicrograph - Alloy No. 2 - pure tin and beta solid solution.

Plate V



Tin-Bismuth Diagram
232°
268°
Liquid
α + Liq.
β + Liq.
135°
α
β
95°
α + β
Sn + β
Sn
Bi



Hardness
(Scleroscope)
12
10
8
6
4
2
0
100
Atomic Percent Bismuth

Fig. 1.--80% Bismuth, 20% Tin - 400x
Plates of tin in matrix of beta solid solution

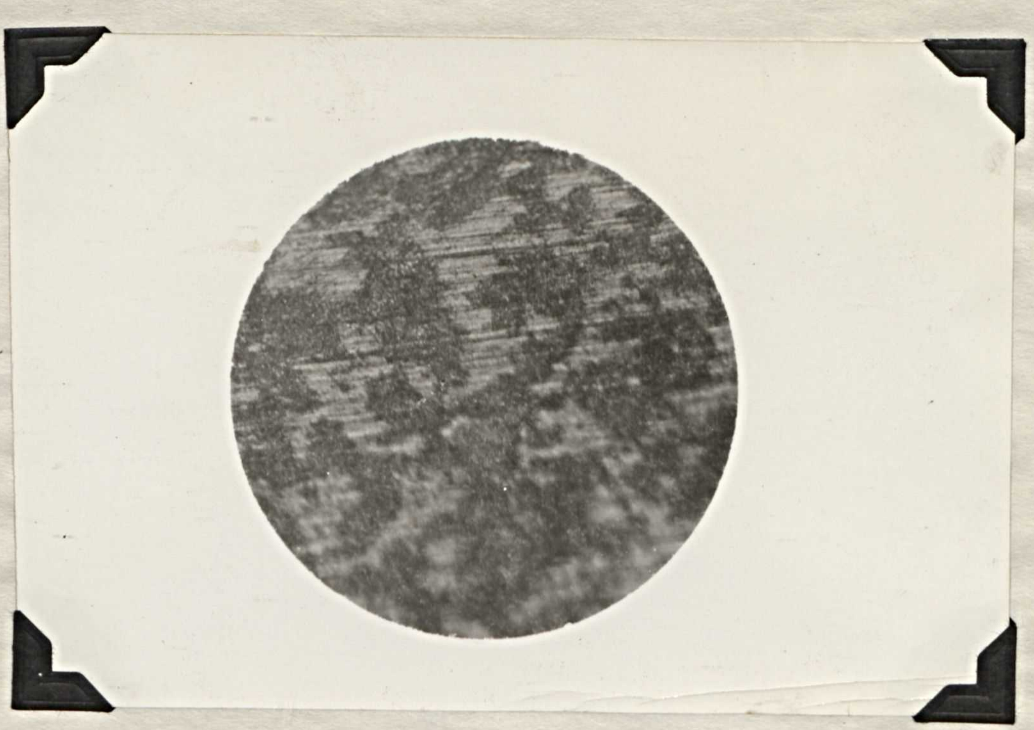


Fig. 2.--20% Tin, 80% Cadmium - 400x
Mixture of beta and delta solid solutions

The Alloys of Cadmium and Tin

Except for those instances in which small quantities of cadmium are added to tin as a means of improving some properties of the puremetal, the alloys of the tin-cadmium system are of little more than theoretical interest. Referring to the equilibrium diagram, Plate VII, we see that the rapidly decreasing power of gamma solid solution to hold cadmium in solution finally ends in a eutectoid inversion at 127° C. The result is the production of beta solid solution (cadmium in tin). At room temperatures, alloys between two and ninety-eight per cent cadmium consist of mixtures of beta and delta solid solutions. Pure cadmium is itself very ductile and malleable and has the faculty of imparting these properties to white metal alloys in which it is used. Conversely, with gold, copper and platinum it yields brittle alloys. Binarily tin and cadmium are of little interest but they are used together quite extensively in termary and quaternary mixtures (with lead and bismuth) for the manufacture of fusible alloys. These two metals are quite similar in properties (both have a "cry" on bending).

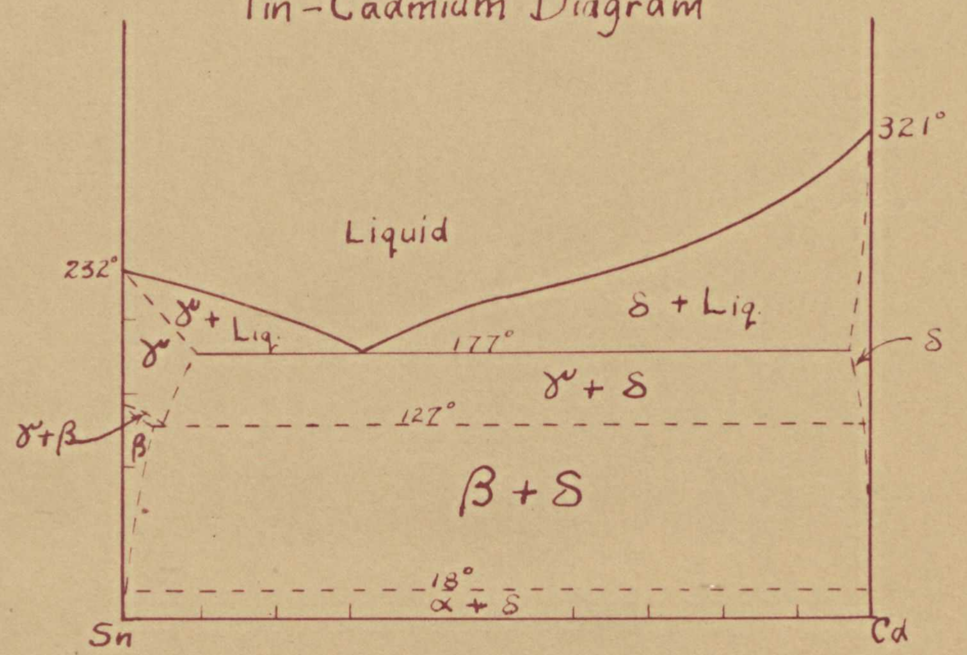
Data:

Alloy No.	Tin %	Cadmium %	Hardness	At.% Cd.
1	20	80	8	81
2	70	30	5	32
3	40	60	9	61

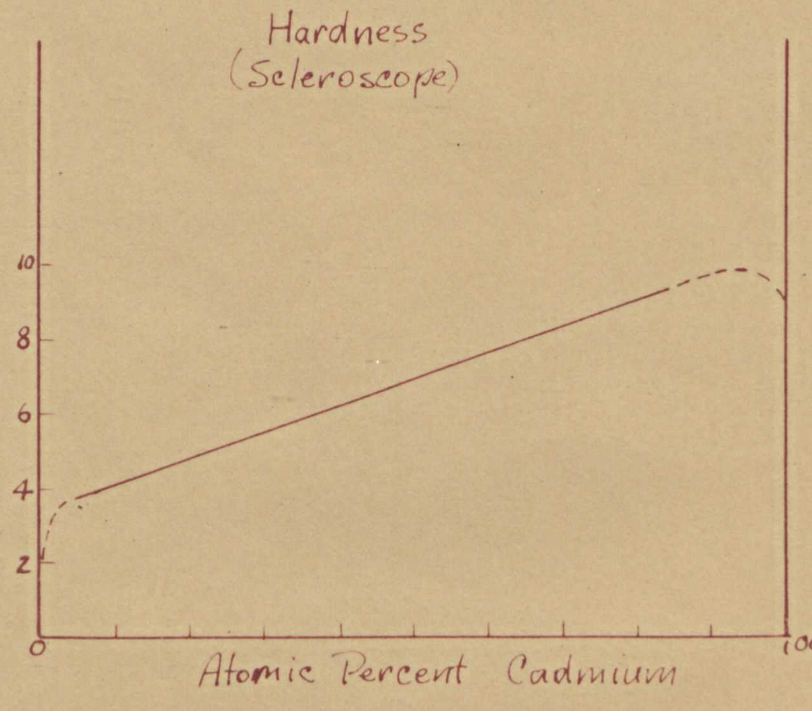
Etchant - 10% Nitric Acid - 3 secs.

Photomicrograph - Alloy No. 1 - beta + delta solid solutions.

Plate VII



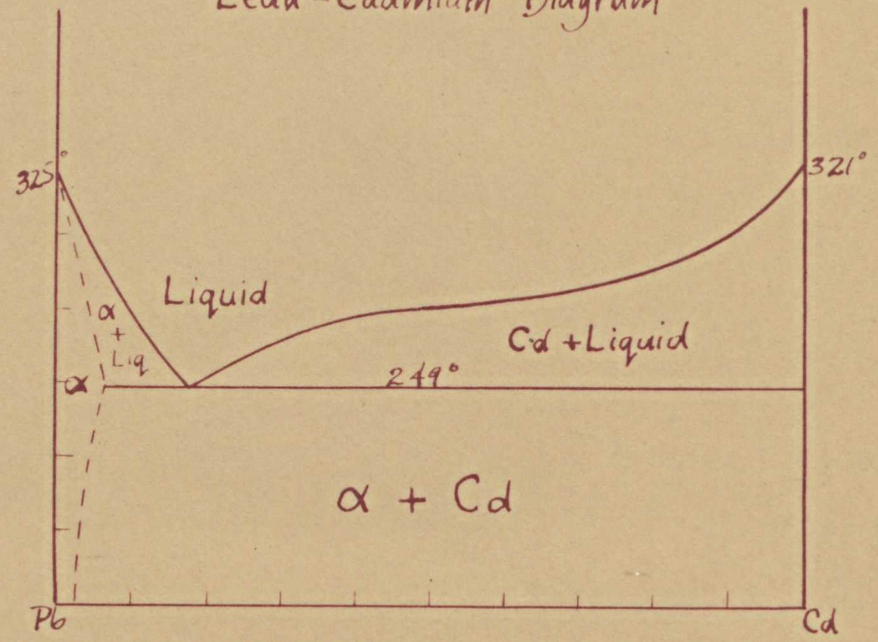
Tin-Cadmium Diagram
321°
Liquid
232°
δ + Liq.
γ + Liq.
177°
δ
γ
γ + δ
γ+β
127°
β
β + δ
18°
α + δ
Sn
Cd



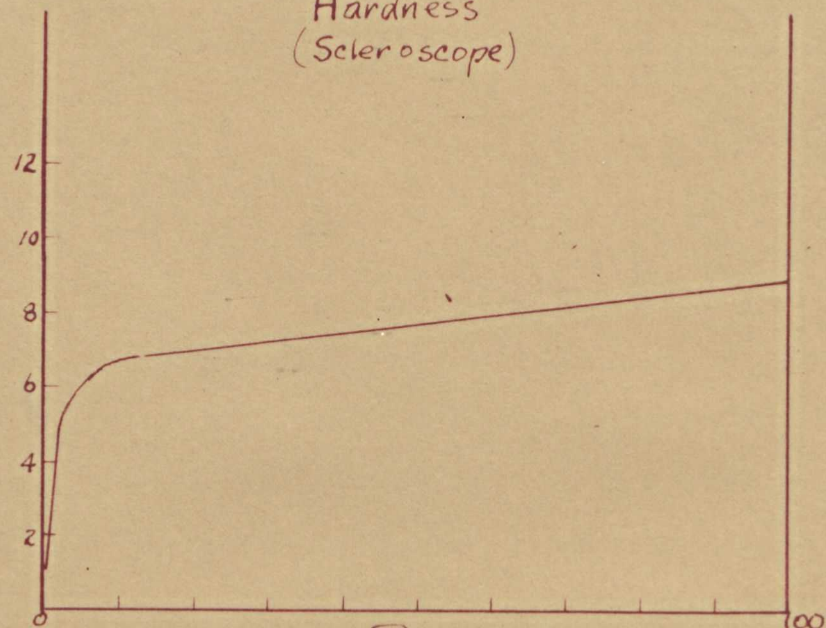
Hardness
(Scleroscope)
10
8
6
4
2
0
100
Atomic Percent Cadmium

Plate VIII

Lead-Cadmium Diagram

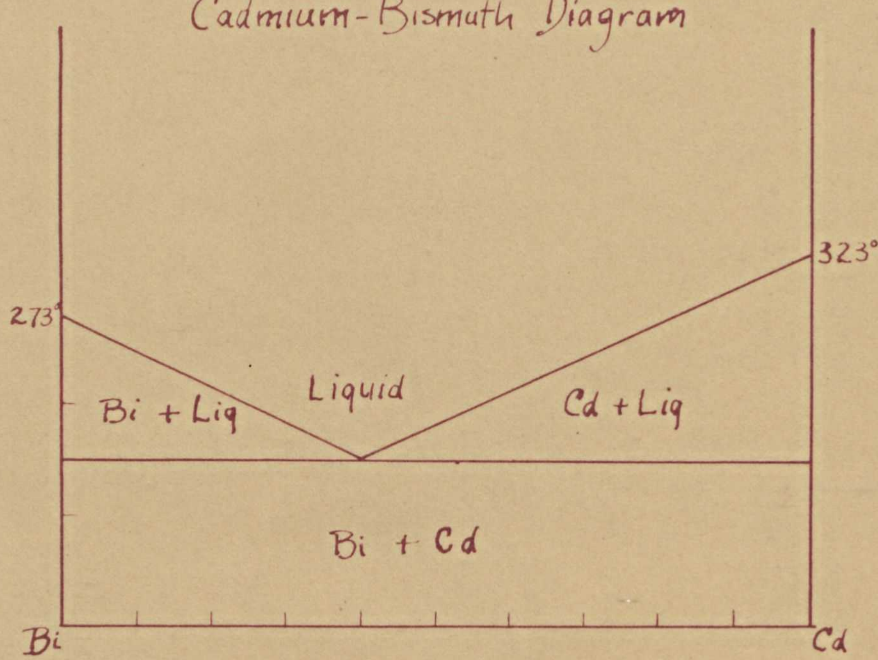


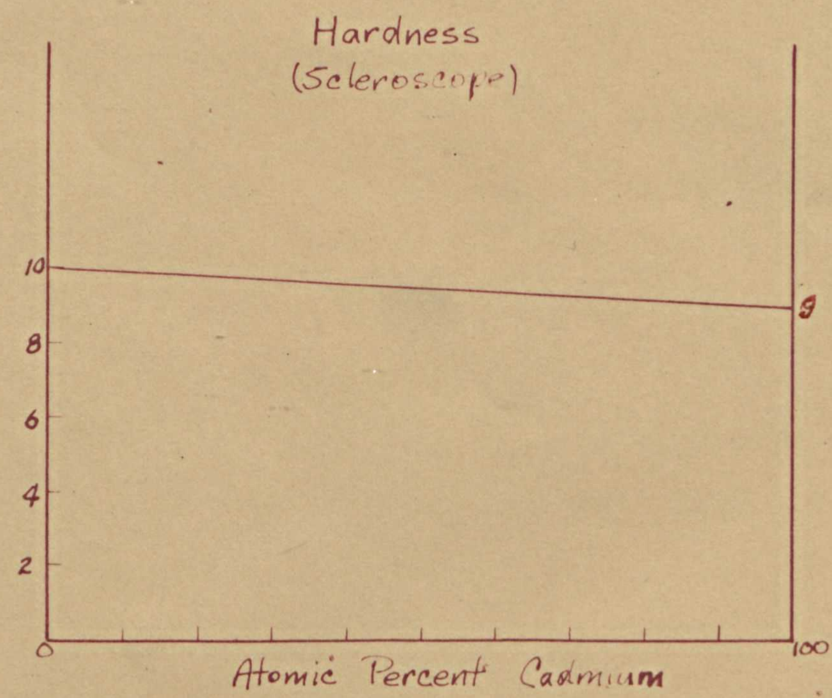
Hardness
(Scleroscope)



Atomic Percent Cadmium

Plate IX


Cadmium-Bismuth Diagram
323°
273°
Liquid
Bi + Liq
Cd + Liq
Bi + Cd
Bi
Cd


Hardness
(Scleroscope)
10
9
8
6
4
2
0
100
Atomic Percent Cadmium

The Alloys of Cadmium and Lead

The alloys of this system are, like those of the tin-cadmium system, of little commercial importance. The combination of these two metals characteristically yields a group of alloys which are very ductile and malleable and which have good casting properties. The equilibrium diagram shows the eutectic at 17.4 per cent cadmium which melts at 249° C. and that although there is a limited solubility of cadmium in lead, there is no solubility of lead in cadmium in the solid state. As mentioned above, these metals are both important constituents of fusible alloys. Cadmium may be said to have a good effect on the properties of lead since it increases the hardness without too great a sacrifice in malleability and ductility.

Data:

Alloy No.	Cadmium %	Lead %	Hardness	At. % Cd.
1	20	80	7	32
2	50	50	8	65
3	2	98	5	3.6

Etchant - 0.8 % silver nitrate - 2 secs.

The Alloys of Cadmium and Bismuth

The equilibrium diagram of the system cadmium-bismuth is of the simple eutectiferous type with no solid solubility at all. The eutectic is at 40% cadmium and melts at 140° C. Small additions of one metal to the other do not seriously affect hardness since there are no solid solutions formed. As always, additions of bismuth cause the alloys to become more and more brittle. Cadmium and bismuth are probably the most important constituents of the very fusible alloys such as Rose's Metal, Lipowitz Metal and Wood's Metal (25% Pb, 50% Bi, 12.5% Cd, 12.5% Sn). The latter melts at only 70° C and finds extensive use not only for control heads in automatic fire extinguishers but also, since it wets glass, as a glass cement which is not attacked by petroleum.

Data:

Alloy No.	Cadmium %	Bismuth %	Hardness	At. % Cd.
1	30	70	9	44.5
2	80	20	10	87.7
3	40	60	9	55

Etchant - 10% Nitric Acid - 5 secs.

SUMMARY AND CONCLUSIONS

The alloys of the white metal group are characterized by their high densities, low melting points (seldom over 400° C) and the very limited solid solubility of the alloys comprising it.

The eutectic alloy and those alloys whose composition approximate equal quantities of each metal are universally harder and stronger than either pure metal, although less malleable and ductile.

In those combinations represented by equilibrium diagrams which show a slight solid solubility, the hardness is increased enormously by small additions until the solution becomes saturated. Thus, assuming that increased hardness is due to a distortion of the space lattice at the points where the solute enters, we may say that the saturated solid solution represents the maximum distortion which the lattice will stand. Accordingly, the hardness produced by a given percentage of a second metal is inversely proportional to the solubility of that metal.

The effect of the rate of cooling may be summarized as follows: slow cooling produces a large grain, a coarse structure and a stronger, but more brittle alloy.

As for other metals and alloys, rolling or other cold work causes the alloys to become stronger and harder.

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